

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification⁵ : C23C 4/00, B32B 33/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/19505 (43) International Publication Date: 1 September 1994 (01.09.94)</p>
<p>(21) International Application Number: PCT/US94/01773 (22) International Filing Date: 18 February 1994 (18.02.94) (30) Priority Data: 08/019,558 19 February 1993 (19.02.93) US (71) Applicant: LEAD INDUSTRIES ASSOCIATION, INC. [US/US]; 295 Madison Avenue, New York, NY 10017 (US). (72) Inventors: SANDUJA, Mohan; 144-90 41st Avenue, Flushing, NY 11355 (US). SUGATHAN, Kenneth; 39 Ross Hall Boulevard South, Piscataway, NJ 18854 (US). KESAVAN, Purshothaman; 864-49th Street, Brooklyn, NY 11220 (US). HOROWITZ, Carl; 5607 Fillmore Avenue, Brooklyn, NY 11239 (US). (74) Agents: ROBINSON, Joseph, R. et al.; Darby & Darby, 805 Third Avenue, New York, NY 10022 (US).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.</p>	
<p>(54) Title: PROTECTIVE COATING FOR LEAD SHEETS</p> <p>(57) Abstract</p> <p>Coated articles are provided which include a lead substrate and a film adhered to the substrate. The film includes a polymer of at least one polymerizable vinyl monomer or a prepolymer thereof; optionally at least one polymerizable epoxy monomer or a prepolymer thereof; optionally at least one polymerizable surfactant monomer; and optionally at least one binder resin. A method for the preparation of these coated articles is also provided. A lead substrate is contacted with a film forming coating composition. The film forming composition is a mixture of at least one polymerizable vinyl monomer or a prepolymer thereof; at least one graft initiator; a solvent; optionally at least one polymerizable epoxy monomer or a prepolymer thereof; optionally at least one polymerizable surfactant monomer; optionally at least one binder monomer or a prepolymer or resin thereof; optionally at least one surfactant which may be the same as or different than the polymerizable surfactant monomer; optionally at least one catalyst; and optionally at least one cross-linking agent. The substrate is then cured.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

5

10

PROTECTIVE COATING FOR LEAD SHEETSFIELD OF THE INVENTION

This invention relates to coated lead articles which are water repellent and resistant to abrasion, wear, chipping, and environmental conditions that have a tendency to degrade or to corrode lead. These coated lead articles are particularly useful in outdoor applications such as roofing materials. A film forming polymer coating is adhered to the lead substrate through a graft polymerization process.

20

BACKGROUND OF THE INVENTION

Lead products and particularly lead sheets are used in numerous indoor and outdoor applications such as in the roofing industry. Although lead is a relatively unreactive material, it is still subject to corrosion and wear due to changes in temperature, pressure, and humidity and due to atmospheric pollutants such as hydrogen sulfite, carbon dioxide, and sulfur dioxide. Furthermore, minute amounts of lead may leach from lead articles subjected to rain or water runoff.

30

Horowitz, in U.S. Patent No. 3,389,848, disclosed polymer grafting onto non-metallic substrates by bonding silver or silver oxide onto the substrate surface and then polymerizing a material to the surface, and in U.S. Patent No. 3,698,931, disclosed the bonding of polymeric materials to silver ion activated non-metallic substrates. See also Horowitz et al., U.S. Patent No. 3,998,602.

Non-metallic high polymeric materials which are difficult to dye were activated and made susceptible to sulfonation with colloidal silver or silver oxide in Horowitz et al, U.S. Patent Nos. 3,880,580 and 2,940,377.

5

Grafting liquids containing silver salts were incorporated to polymerize and simultaneously graft monomers onto hydrocarbon liquids in Horowitz, U.S. Patent No. 3,929,800.

10

An adhesive that includes elastomers, a prepolymer or a polymerizable monomer, and a graft initiator has also been used to secure elastomer substrates together by Horowitz et al., U.S. Patent No. 4,051,090.

15

A method for protecting alumina and aluminium alloys by the chemical bonding of a polymerized coating to aluminium oxide on the aluminium surface was disclosed by Horowitz et al., U.S. Patent No. 4,105,811. Silver ion acts as an initiator and is regenerated during the polymerization by a peroxide catalyst.

20 Steel articles are coated with polymeric fibers containing fillers in Horowitz, et. al., U.S. Patent No. 4,106,955. See also Dichter, U.S. Patent No. 4,421,569.

25

Paints that include a polymerizable vinyl monomer, an epoxy prepolymer, a urethane resin, a peroxide polymerization initiator, a silver graft initiator, and a solvent are applied to steel or aluminium metal articles, plastic articles, and ceramic articles by Horowitz et al., U.S. Patent No. 4,107,028.

30

Pigment dispersions were chemically grafted with vinyl and/or acrylic monomers to nitrocellulose by Horowitz et al., U.S. Patent No. 4,683,007, and whole monomers and germicides were grafted onto activated carbon in U.S. Patent Nos. 4,898,676 and 4,966,872 to Horowitz et al.

35

Wiedeman et al., U.S. Patent No. 5,043,226, disclose the grafting of a coating on steel, aluminium, iron, platinum, silver, nickel, gold, cobalt, copper, or copper alloy substrates. The coating is prepared from polymerizable monomers having at least two functionalities, graft initiators containing nickel ion, and a reduction agent capable of reducing nickel ion to nickel metal.

Scheinfeld, Polymer News, Vol. II, Nos. 11/12, pp. 19-24 describes generally the possibility of grafting polymers to substrates including lead, but specific graft initiators and polymeric film components are not provided.

It has now been discovered that polymer-based coatings can be chemically bonded to lead substrates, thereby protecting the substrate from degradation.

SUMMARY OF THE INVENTION

Coated articles have now been prepared which comprise:
(A) a substrate comprising lead; and (B) a film adhered to the substrate. The film comprises:

- (a) a polymer of
 - (i) at least one polymerizable vinyl monomer or a prepolymer thereof;
 - (ii) optionally at least one polymerizable epoxy monomer or a prepolymer thereof; and
 - (iii) optionally at least one polymerizable surfactant monomer; and
- (b) optionally at least one binder resin which may be the same as or different than said polymerizable epoxy.

In a preferred embodiment, the vinyl monomer has at least one functional group in addition to the vinyl group.

A method for the preparation of these coated articles has also been discovered. A lead substrate is contacted with a film forming coating composition. The film forming composition comprises a mixture of:

- 5 (a) at least one polymerizable vinyl monomer or a prepolymer thereof;
- (b) at least one graft initiator;
- (c) a solvent;
- (d) optionally at least one polymerizable epoxy
- 10 monomer or a prepolymer thereof;
- (e) optionally at least one polymerizable surfactant monomer;
- (f) optionally at least one binder monomer or a prepolymer or resin thereof which may be the same as or different
- 15 than said polymerizable epoxy;
- (g) optionally at least one surfactant which may be the same as or different than the polymerizable surfactant monomer;
- (h) optionally at least one catalyst; and
- 20 (i) optionally at least one cross-linking agent. The substrate is then cured.

Also contemplated by the present invention are film forming compositions comprising the mixture above and

25 particularly in the form of an emulsion.

DETAILED DESCRIPTION OF THE INVENTION

The coated articles of the present invention comprise a coating adhered to a lead containing substrate. Preferably,

30 the article and/or substrate are in the form of a sheet or a tile which may be used as a roofing material. The substrate may be coated on all of its surfaces or may be coated on fewer than all of its surfaces.

The coating is in the form of a film which includes at least one polymer that is adhered to the substrate, preferably through chemical bonding and most preferably through chemical grafting. This polymer can be homopolymeric or copolymeric and is polymerized from at least one polymerizable vinyl monomer or a prepolymer thereof.

Although any polymerizable vinyl monomer is suitable for use in the film, preferred vinyl monomers are polyfunctional, i.e. substituted with one or more functional groups in addition to the vinyl group. Functional groups are groups that have replaced a hydrogen on the monomer and through which a bond can be formed. A monomer that has more than one functional group in addition to the vinyl group has more than one hydrogen atom replaced. This allows the monomer to form a bond through each of the functional groups and/or through the vinyl group. The monomers may be substituted with one or more hydroxy, carboxy, glycidyl, aziridinyl group, or any combination thereof. Most preferred vinyl monomers are substituted or unsubstituted acrylic monomers or esters or salts thereof. These acrylics include, but are not limited to, mono-, di-, and tri-acrylics such as hydroxylated triacrylates such as Sartomer SR 9035.

Polymerizable epoxy monomers or prepolymers thereof are optional components of the polymer. Suitable epoxy monomers include, but are not limited to, aliphatic, cycloaliphatic, and aromatic epoxy monomers, and particularly those having more than one epoxy group per molecule. Typical aliphatic epoxy monomers include, but are not limited to, 1,4 butane diol diglycidyl ether. Typical cycloaliphatic epoxy monomers include, but are not limited to, 3,4-epoxy cyclohexylmethyl (3,4-epoxy) cyclohexane carboxylate and bis (3,4-epoxy-6-methyl-cyclohexylmethyl) acrylate. Typical aromatic epoxy monomers include, but are not limited to, diglycidyl ethers of polyphenol

epoxy such as bisphenol A, resorcinol diglycidyl ether epoxy and phenol-formaldehyde novolac polyglycidyl ether epoxy.

Polymerizable surfactant monomers are also optional
5 components of the polymer and are preferably non-ionic surfactants including, but not limited to, sodium styrene sulfonate and sodium vinyl sulfonate.

Furthermore, the polymer can be cross-linked with
10 cross-linking agents that are known to those skilled in the art, including, but not limited to, polyfunctional aziridines.

The film can also include one or more binder resins that aid in coalescing the film. Such binder resins may be
15 polymerizable with the polymers above or may be blended with the monomers in the film coating formulation. Preferably, the binder resin is an acrylic resin, an epoxy resin, a urethane resin, or any combination thereof. Preferred urethanes are urethanes formed by the reaction of either a polyester or a polyether with
20 an aromatic or aliphatic diisocynate. They may be vulcanized through the isocynate group by reaction with glycols, diamines, diacids, or amino alcohols. Preferred urethanes are derived from aliphatic diisocynates, and most preferably have from 0 to about 6% reactive-NCO- groups.

25

Other components that may be blended in the coating composition, and consequently in the film, include, but are not limited to, ultraviolet radiation inhibitors including, but not limited to, substituted hydroxy/phenol benzotriazoles; flame
30 retardants; abrasion improving agents; lubricants; soil repellency enhancing agents; adhesion promoting agents; water absorbency enhancing agents; gas permeability enhancing agents; biocides; thixotropes; or the like.

Typically, the coating will be from about 0.1 to about 260 microns in thickness, will have a pencil hardness of about 3B, and will have a specular gloss value of from about 20 to about 70.

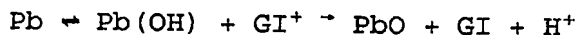
5

The coated articles of the present invention are prepared by contacting a lead substrate with a film forming composition and subsequently curing the article. In addition to the polymerizable vinyl monomer(s) or prepolymer(s), preferably
10 in the form of an emulsion, the optional polymerizable epoxy monomer(s) or prepolymer(s), and the optional polymerizable surfactant monomer(s), the film forming composition mixture includes at least one graft initiator and a solvent.

15

Suitable graft initiators include iron (i.e., Fe^{++} or Fe^{+++}), silver (i.e., Ag^+), cobalt (i.e., Co^{++}), and/or copper (i.e., Cu^{++}) salts, such as nitrates, perchlorates, acetates, sulfates, or any combination thereof. Preferably, the graft initiator is an iron salt and most preferably is ferrous salt
20 such as ferrous sulfate.

While not intending to be bound by any theory, applicants hypothesize that in the presence of initiator, a thin layer of oxide and hydroxyl groups is firmly bound to the lead
25 substrate. The graft initiator ("GI⁺") removes the hydrogen of the hydroxyl group to form a radical which reacts with the film forming polymerizable monomer(s) or prepolymer(s). The oxides in hydroxyl groups react with the functional groups of the monomer(s) and/or prepolymer(s) to initiate a polymerization
30 reaction on the surface of the substrate. This reaction is illustrated below:

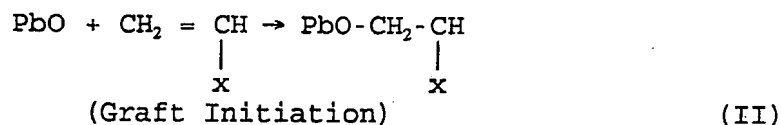


35

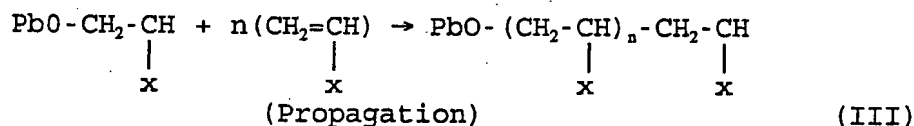
(Radical Formation)

(I)

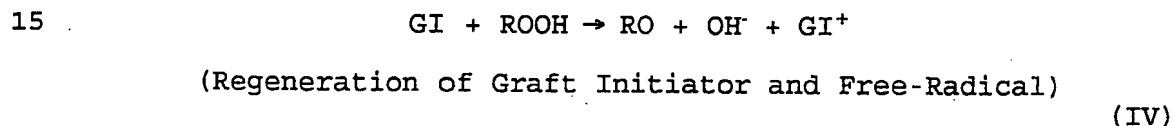
8



5



10



15

20

Reaction (I) provides a radical site on the lead substrate by the reduction of the ion of the graft initiator and oxidation of the substrate. Reactions (II) and (III) illustrate the grafting of an exemplary vinyl monomer to the metallic substrate at the oxidized site to form a lead-graft polymer radical on the substrate and the propagation of this graft polymer. Reaction (IV) illustrates the regeneration of the graft initiation ion by the presence of a peroxide in the film forming composition mixture.

25

30

Although the film forming mixture may include an aqueous or organic solvent, an aqueous solvent is preferred. Typically, one or more surfactants are added to the mixture to prepare an emulsion. Non-polymerizable or polymerizable surfactants are suitable and non-ionic surfactants are preferred. Polymerizable surfactants are those having one or more vinyl groups including, but not limited to, sodium vinyl sulfonate and/or sodium styrene sulfonate.

35

40

Optional catalysts include persulfates including, but not limited to, ammonium persulfate or peroxide-type catalysts including, but not limited to, hydrogen peroxide, methyl ethyl

ketone peroxide, tert-butyl hydroperoxide, di-tert-butyl peroxide, benzyl peroxide, di-cumyl peroxide, lauroyl peroxide, tert-butyl per-benzoate, iodine peroxide, peracetic acid, and most preferably, urea peroxide.

5

The polymer film forming mixture optionally includes a cross-link agent as described above. The binder resins are as described above and, typically, are added in the form of an aqueous emulsion as well. The mixture is prepared in conventional mixing equipment as known to those skilled in the art. Although the order of addition of the components of the film forming composition is not believed to be significant, when optional components are used, it is preferred that the vinyl and/or epoxy monomer or prepolymer, the binder, and the solvent are mixed before any other components are added. Then, all additives other than cross-linker can be added as a premix along with the catalyst. Finally, the cross-linker can be added.

The substrate may be cleaned before contact with the film forming mixture. It may also be moistened with water, although this is not necessary. Atmospheric moisture would be sufficient to form any oxide or hydroxyl groups, if necessary.

The amount of polymerizable vinyl monomer(s) or prepolymer(s) in the film forming composition is that amount effective to form a water repellant coating, and generally ranges from about 0.005 to about 10 parts by weight based upon 100 parts by weight of the film forming composition.

The amount of graft initiator in the film forming composition is that amount effective to initiate grafting of the polymerizable monomer(s) or prepolymer(s) to the substrate and, typically, ranges from about 0.005 to about 0.1 part by weight based upon 100 parts by weight of the polymerizable vinyl monomer(s) and/or prepolymer(s). Preferably, the amount of graft

initiator ranges from about 0.01 to about 0.05 part by weight on this basis, and most preferably ranges from about 0.02 to about 0.03 part by weight on this basis.

5 The amount of solvent in the film forming composition typically ranges from about 10 to about 99.99 parts by weight based upon 100 parts by weight of film forming composition.

10 The amount of binder resin is that amount effective to enhance the rate that the film coalesces and preferably ranges from 0 to about 99 parts by weight based upon 100 parts by weight of film forming composition.

15 The amount of optional catalyst typically ranges from 0 to about 25 parts by weight based upon 100 parts by weight of polymerizable vinyl monomer(s) and preferably ranges from about 0.1 to about 20 parts by weight based upon 100 parts by weight on the same basis.

20 The amount of optional cross-linker typically ranges from about 25 to about 500 parts by weight based upon 100 parts by weight of polymerizable monomer(s) or prepolymer(s).

25 The film forming composition is applied by methods known to those skilled in the art including, but not limited to, dipping, spraying, roller coating, brushing, or the like. The article is cured by drying at ambient conditions or at elevated temperatures of up to about 275°C or higher. The coating formulation should be dry before the coated substrate is used.

30 Coating thickness can be varied by varying the time of application of the coating, the amount applied in a single coating, or the number of coatings.

35

DESCRIPTION OF THE PREFERRED EMBODIMENT

The following examples serve to illustrate the invention. All function percentages are given by weight unless otherwise indicated.

5

EXAMPLE 1

100 parts of binder resin (acrylic prepolymer emulsion - Rhoplex AC 1803 - Rohm & Hass Company - Philadelphia, PA), 10 parts of surfactant monomer (10% sodium styrene sulfonate in water), 10 parts of a second surfactant monomer (25% sodium vinyl sulfonate in water), 0.05 part of graft initiator (0.1% ferrous sulfate in water), 0.1 part of vinyl monomer (hydroxylated triacrylate - Sartomer SR 9035), and 0.01 part of catalyst (urea peroxide) were mixed. The mixture was applied to a lead sheet substrate by brushing. The coated substrate was allowed to dry in air at ambient conditions. The resultant coating was water resistant.

20

EXAMPLE 2

200 parts of binder resin (aliphatic urethane emulsion - NeoRezR-966), 0.5 part of vinyl monomer (hydroxylated triacrylate - Sartomer SR 9035), 40 parts of solvent (deionized water), and 0.1 part of graft initiator (0.1% ferrous sulfate in water) were mixed.

25

A premix of ultraviolet radiation inhibitor (substituted hydroxy/phenyl benzotriazole - Tinvim 1130), 0.7 part of solvent (butyl cellosolve), and 0.7 part of solvent (deionized water) was mixed with the mixture above. 0.1 part of catalyst (urea peroxide) was added, and subsequently, 0.4 part of cross-linker (polyfunctional aziridine - CX-100) was added with agitation.

30

A lead sheet substrate was coated by brushing, and the coated substrate was air dried at ambient conditions. The coating displayed excellent water resistance.

5

EXAMPLE 3

A coating composition was prepared according to the procedure of Example 2. A lead sheet substrate was coated by brushing and was cured at 250-260°C for 30 minutes. The coating displayed excellent water resistance.

10

EXAMPLE 4

The procedure of Example 2 was followed omitting the UV inhibitor, substituting 2.4 parts of butyl cellosolve for the butyl cellosolve, and substituting two parts of the cross-linker for the cross-linker.

A lead sheet substrate was coated by brushing and dried in air. The coated substrate dried faster than that in Example 2. Samples coated with this formulation had excellent water resistance.

20

The above-mentioned patents, publications, and test methods are incorporated herein by reference.

25

Many variations of the present invention will suggest themselves to those skilled in the art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

30

WHAT IS CLAIMED IS

- 1 1. A coated article comprising:
2 (A) a substrate comprising lead; and
3 (B) a film adhered to said substrate, said film
4 comprising:
5 (a) a polymer of
6 (i) at least one polymerizable vinyl
7 monomer or a prepolymer thereof;
8 (ii) optionally at least one
9 polymerizable epoxy monomer or a
10 prepolymer thereof; and
11 (iii) optionally at least one
12 polymerizable surfactant monomer;
13 and
14 (b) optionally at least one binder resin
15 which may be the same or different than
16 said polymerizable epoxy.
- 17 2. A coated article as defined in claim 1, wherein
18 said vinyl monomer has at least one functional group in addition
19 to the vinyl group.
- 1 3. A coated article as defined in claim 2, wherein
2 said vinyl monomer is a substituted or unsubstituted acrylic
3 monomer or an ester or salt thereof.
- 1 4. A coated article as defined in claim 3, comprising
2 a sheet.
- 1 5. A coated article as defined in claim 3, comprising
2 a tile.
- 1 6. A coated article as defined in claim 3, wherein
2 said substrate comprises a sheet.

1 7. A coated article as defined in claim 3, wherein
2 said substrate comprises a tile.

1 8. A coated article as defined in claim 3, wherein
2 said polymer of said film is chemically bonded to said substrate.

1 9. A coated article as defined in claim 8, wherein
2 said polymer of said film is grafted to said substrate.

1 10. A coated article as defined in claim 3, wherein
2 said acrylic monomer or ester or salt thereof is substituted with
3 one or more hydroxy group, carboxy group, glycidyl group, or any
4 combination thereof.

1 11. A coated article as defined in claim 3, wherein
2 said binder resin comprises a urethane resin.

1 12. A coated article as defined in claim 3, wherein
2 said urethane is polymerizable with said polymerizable vinyl
3 monomer or prepolymer.

1 13. A coated article as defined in claim 3, wherein
2 said film further comprises at least one:

3 (d) surfactant which is the same as or different
4 than said polymerizable surfactant monomer;

5 (e) ultraviolet radiation inhibitor;

6 (f) flame retardant;

7 (g) abrasion improving agent;

8 (h) lubricant;

9 (i) water repellency enhancing agent;

10 (j) adhesion promoting agent;

11 (k) water absorbency enhancing agent;

12 (l) gas permeability enhancing agent;

13 (m) biocide; or

14 (n) thixotrope.

1 14. A coated article as defined in claim 3, wherein
2 said film ranges from about 0.1 to about 260 microns in
3 thickness.

1 15. A coated article as defined in claim 3, wherein
2 said film has a pencil hardness of about 3B and a specular gloss
3 value ranging from about 20 to about 70.

1 16. A method of coating an article, said method
2 comprising:
3 (A) contacting a substrate comprising lead with
4 a film forming mixture comprising:
5 (a) at least one polymerizable vinyl
6 monomer or a prepolymer thereof,
7 (b) at least one graft initiator;
8 (c) a solvent;
9 (d) optionally at least one polymerizable
10 epoxy monomer or a prepolymer thereof,
11 (e) optionally at least one polymerizable
12 surfactant monomer,
13 (f) optionally at least one binder monomer,
14 or a prepolymer or resin thereof which
15 may be the same or different than said
16 polymerizable epoxy;
17 (g) optionally at least one surfactant
18 which may be the same as or different
19 than said polymerizable surfactant
20 monomer;
21 (h) optionally at least one catalyst; and
22 (i) optionally at least one cross-linking
23 agent; and
24 (B) curing said article.

25 17. A method as defined in claim 16, wherein said
26 vinyl monomer has at least one functional group in addition to
27 the vinyl group.

1 18. A method as defined in claim 17, wherein said
2 vinyl monomer is a substituted or unsubstituted acrylic monomer
3 or an ester or a salt thereof.

1 19. A method as defined in claim 18, wherein said
2 article comprises a sheet.

3 20. A method as defined in claim 19, wherein said
4 article comprises a tile.

5 21. A method as defined in claim 19, wherein said
6 substrate comprises a sheet.

7 22. A method as defined in claim 18, wherein said
8 substrate comprises a tile.

9 23. A method as defined in claim 18, wherein said
10 substrate is exposed to moisture before said contacting step (A).

1 24. A method as defined in claim 18, wherein said
2 acrylic monomer or ester or salt thereof is substituted with one
3 or more hydroxy group, carboxy group, glycidyl group, or any
4 combination thereof.

1 25. A method as defined in claim 18, wherein said
2 binder resin comprises a urethane resin.

1 26. A method as defined in claim 18, wherein said
2 urethane is polymerizable with said polymerizable vinyl monomer
3 of prepolymer.

1 27. A method as defined in claim 18, wherein said
2 graft initiator is selected from the group consisting of salts of
3 iron, silver, cobalt, copper, or any combination thereof.

1 28. A method as defined in claim 27, wherein said salt
2 is selected from group consisting of nitrates, perchlorates,
3 acetates, sulfates, or any combination thereof.

1 29. A method as defined in claim 28, wherein said
2 graft initiator is an iron salt.

1 30. A method as defined in claim 29, wherein said iron
2 salt is a ferrous salt.

1 31. A method as defined in claim 30, wherein said
2 ferrous salt is ferrous sulfate.

1 32. A method as defined in claim 18, wherein said
2 solvent is an organic solvent.

1 33. A method as defined in claim 18, wherein said
2 solvent is water.

1 34. A method as defined in claim 18, wherein said
2 vinyl monomer or prepolymer is an aqueous emulsion.

1 35. A method as defined in claim 18, wherein said
2 binder is an aqueous emulsion.

1 36. A method as defined in claim 18, wherein said film
2 forming mixture is an aqueous emulsion.

1 37. A method as defined in claim 18, wherein said
2 surfactant monomer is a nonionic surfactant.

1 38. A method as defined in claim 18, wherein said
2 catalyst is a peroxide catalyst.

1 39. A method as defined in claim 38, wherein said
2 catalyst is urea peroxide.

1 40. A method as defined in claim 18, wherein said
2 cross-linking agent is a polyfunctional aziridine.

1 41. A method as defined in claim 18, wherein said
2 contacting is by dipping, spraying, roller-coating, brushing, or
3 any combination thereof.

1 42. A method as defined in claim 18, wherein said
2 coated article is cured at ambient conditions.

1 43. A method as defined in claim 18, wherein said
2 coated article is cured at elevated temperature.

1 44. A film forming composition comprising:
2 (a) at least one polymerizable vinyl
3 monomer or a prepolymer thereof,
4 (b) at least one graft initiator;
5 (c) a solvent;
6 (d) optionally at least one polymerizable
7 epoxy monomer or a prepolymer thereof,
8 (e) optionally at least one polymerizable
9 surfactant monomer,
10 (f) optionally at least one binder monomer,
11 or a prepolymer or resin thereof which
12 may be the same or different than said
13 epoxy monomer or prepolymer;
14 (g) optionally at least one surfactant
15 which may be the same as or different

16 than said polymerizable surfactant
17 monomer;
18 (h) optionally at least one catalyst; and
19 (i) optionally at least one cross-linking
20 agent.

1 45. A product prepared by the method of claim 19.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/01773

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C23C 4/00; B32B 33/00.

US CL : 428/413, 463, 921; 427/372.2, 386, 388.1, 388.2, 388.4, 368, 359.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/413, 463, 921; 427/372.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5,043,226 (WIEDEMAN et al) 27 AUGUST 1991, See Abstract.	1-45
A	US, A, 4,421,569 (DICHTER et al) 20 December 1983. See Abstract.	1

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

25 APRIL 1994

Date of mailing of the international search report

16 MAY 1994

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Authorized officer

EDITH BUFFALOW

Facsimile No. (703) 305-3230

Telephone No. (703) 308-2351